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(54) ION-CROSSLINKING FILM AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an ion-crosslinking film excellent in biodegradability and recycling properties and excellent in film strength.

SOLUTION: This biodegradable ion cross-linking film is constituted of a polysaccharide having a carboxyl group and polyvalent metal ions for cross- linking the carboxyl groups. The equivalent ratio of the polyvalent metal ion to the carboxyl group is (0.061/1)-(0.11/1). The polysaccharide can be a water soluble polysaccharide and the polyvalent metal ion can be a divalent metal ion, etc. The ion cross-linking film is produced by casting and drying the mixture of a polysaccharide and a metal compound with water.

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DETAILED DESCRIPTION

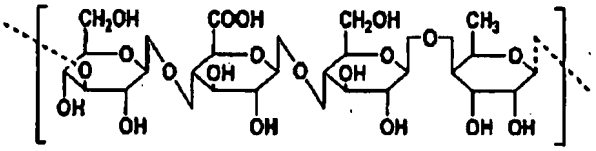
[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the ion bridge formation film which is biodegradability and can be recycled, and its manufacture approach.
[0002]
[Description of the Prior Art] synthetic macromolecule -- the chemical stability sake -- being various (for example, film processing etc.) -- it is used. Since much of such synthetic macromolecules are not disassembled in a nature, the trash is the cause which causes an environmental problem. From such a background, development of the plastics (biodegradable plastic) decomposed in a nature is attracting attention in consideration of harmony with nature in recent years.
[0003] As a biodegradable plastic, the products (for example, plastic film etc.) using the synthetic macromolecules (polysaccharide etc.) which have naturally-ocurring polymers and its similar structure are developed. However, a moldability is also low while it is difficult to give properties, such as reinforcement (breaking strength etc.), when carrying out film shaping of such a macromolecule.
[0004] On the other hand, there is a macromolecule bridge formation film etc. among the films to which reinforcement was made to increase. However, since the bridge formation film consists of macromolecules which constructed the bridge by covalent bond, its biodegradability is low. Moreover, a remolding is difficult and recycle nature also has it.
[low]
[0005] The method of making a macromolecule construct a bridge according to ion bridge formation is reported (Carbohydrate Polymers, Vol.29, No.1, p.p.11-16, 1996). By this reference, ion bridge formation of GERANGERU was carried out by 1 or divalent cations (calcium cation etc.), the reinforcement of gel is improved, and it is indicated that the reinforcement of gel serves as [the ratio ([cation] / [COO-]) of a cation and the carboxyl group which GERANGERU has] max in the 0.5 to 1 neighborhood.
[0006]
[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is to offer the ion bridge formation film excellent in biodegradability and recycle nature, and

its manufacture approach.
[0007] Even if other purposes of this invention have the little rate of a metal ion to carboxyl group content polysaccharide, they are to offer the ion bridge formation film excellent in film reinforcement, and its manufacture approach.
[0008]
[Means for Solving the Problem] In order to attain said purpose, wholeheartedly, this invention persons found out that the reinforcement of a film could be greatly improved if the metallic compounds of a minute amount are added to carboxyl group content polysaccharide as a result of examination, and completed this invention.
[0009] That is, the ion bridge formation film of this invention consists of polysaccharide which has a carboxyl group, the bridge is constructed over said carboxyl group with polyvalent metal ion, and the equivalent ratio of said polyvalent metal ion to said carboxyl group is 0.061 / 1 - 0.11/1. Moreover, said ion bridge formation film is biodegradability. Said polysaccharide may be water-soluble polysaccharide etc. and polyvalent metal ion may be a divalent metal ion etc.
[0010] The polysaccharide which has a carboxyl group, water dissociative or an ionic dissociation nature polyvalent metal compound, and mixture with water are cast for this invention, and the manufacture approach of the ion bridge formation film to dry is also included in it.
[0011] In addition, "water dissociative metallic compounds" means the compound "ionic dissociation nature metallic compounds" which dissolves in the aquosity solvent containing water or water, and produces a metal ion among this specification.
[0012]
[Embodiment of the Invention] The ion bridge formation film of this invention consists of polysaccharide which has a carboxyl group, and the bridge is constructed over said carboxyl group with polyvalent metal ion. Therefore, said ion bridge formation film has high biodegradability. Moreover, since ion bridge formation is carried out, heating can cancel ionic bond and it can recycle easily with hot forming.
[0013] As said polysaccharide, especially as long as it has a carboxyl group, it is not restricted, but various base polysaccharide (homoglycan, heteroglycan, etc.) can be used. As said homoglycan, glucan (a cellulose, starch, glycogen, a trichosanthes seed, a laminaran, dextran, etc.), fructans (an inulin, levan, etc.), mannans (ZOUGE coconut mannan etc.), xylans (xylan of rice straw etc.), galacturonan (pectic acid etc.), MANNURONAN (alginic acid etc.), N-acetyl glucosamine polymers (chitin etc.), these derivatives, etc. can be illustrated. As said heteroglycan, diheteroglycan (GUARAN, the mannan of konnyaku, heparin, chondroitin sulfate, hyaluronic acid, etc.), TORIHETEROGURIKAN (vegetable mucilages, such as GERANGAMU, mess kit gum, and GATCHIGAMU, gum, bacteria polysaccharide, etc.), tetra-heteroglycans (mucilages, such as gum arabic, gum, bacteria polysaccharide, etc.), these derivatives, etc. can be illustrated.
[0014] polysaccharide -- everything but a carboxyl group -- for example, -SO3 H, -OSO3 H, and -H2 PO4 You may have the anionic radical. etc. -- Furthermore, you may have hydrophilic radicals, such as -NH2, -CN, -OH, -NHCONH2, -(OCH2 CH2)-, -NR3 X (here, R shows an alkyl group and X shows a halogen atom), SO3 NH2 CO-, and -N(SO3H)-.
[0015] In many cases, said carboxyl group content polysaccharide is water solubility, and

its water-soluble polysaccharide is desirable. As an example of said polysaccharide, GERANGAMU, a carboxyl group content cellulose [carboxymethyl radical content cellulose for example, a carboxymethyl cellulose (CMC) and carboxymethyl methyl cellulose -- Carboxy methyl ethyl cellulose, carboxymethyl hydroxyethyl cellulose, carboxymethyl hydroxypropylcellulose etc. -- etc. --] and carboxyl group content starches (carboxymethyl starch (CMS) etc.) -- A pectic acid and its derivatives (pectic-acid sodium etc.), an alginic acid, its derivatives (sodium alginate etc.), etc. are mentioned. these polysaccharide -- a kind -- or two or more sorts can be used, combining. GERANGAMU is desirable among these polysaccharide. GERANGAMU is for example, the following type (1). It has the unit expressed.

[0016]

[Formula 1]



(1)

[0017] Such GERANGAMU is used as a food additive and its safety is also high while it is the outstanding gelling agent. Therefore, unless a bridge is especially constructed with a harmful metal ion, even if biodegradation of the film containing GERANGAMU is carried out, it is harmless.

[0018] especially the content of a carboxyl group is restricted in said carboxyl group content polysaccharide -- not having -- for example, per [0.05-3 (for example, 0.1-3)] anhydrous glucose radical 1 unit -- it can choose from about 0.1 to two range preferably.

[0019] the average degree of polymerization n of polysaccharide -- 10-20,000 (for example, 50-20,000) -- desirable -- 100-20,000 (for example, 100-15,000) -- it is 400 to about 10,000 still more preferably.

[0020] Especially as long as a bridge can be constructed as polyvalent metal ion in the carboxyl group which said polysaccharide has, it is not restricted, but 2 - tetravalent (especially trivalent [2 - trivalent]) extent and a desirable divalent metal ion can be used. As said metal ion, alkaline earth metals (Magnesium Mg, Calcium calcium, Strontium Sr, barium Ba, etc.), periodic-table 8 group metals (Iron Fe, ruthenium Ru, etc.), periodic-table 11 group metals (copper Cu etc.), periodic-table 12 group metals (zinc Zn etc.), periodic-table 13 group metals (aluminum aluminum etc.), etc. can be illustrated. As a divalent metallic ion, Mg2+, calcium2+, Sr2+, Ba2+, Cu2+, Zn2+, etc. can be illustrated, and ion, such as aluminum3+ and Fe3+, can be illustrated as a trivalent metallic ion. said metal ion -- a kind -- or two or more sorts can be used, combining. Especially a desirable metal ion is the cation of alkaline earth metals, such as Mg2+ and calcium2+, and can obtain an ion cross-linking film with high biodegradability and safety by using such a metal ion.

[0021] As water dissociative metallic compounds which are the ion source of said polyvalent metal ion The salt of the metal which constitutes said metal ion, for example, a halogenide ; An inorganic-acid salt, (For example, chlorides, such as a magnesium chloride and a calcium chloride) For example, a fault halogen acid salt (for example, perchlorates, such as magnesium perchlorate and perchloric acid calcium etc.), A sulfate (for example, magnesium sulfonate, calcium sulfonate, etc.), Nitrates (for example, a

magnesium nitrate, a calcium nitrate, etc.), phosphate (for example, magnesium phosphate, calcium phosphate, etc.); an organic-acid salt (for example, acetate, such as magnesium acetate and calcium acetate etc.), for example, carboxylate etc., is mentioned. these metallic compounds are independent -- or two or more sorts can be used, combining. The chloride of said metal, a sulfate, a nitrate, acetate, etc. are desirable among these compounds.

[0022] In addition, as long as it is required, univalent metal ion, such as alkali-metal ion (lithium ion Li+, sodium ion Na+, potassium ion K+, caesium ion Cs+, etc.), may be used together.

[0023] The reinforcement of a film is high even if the rate of a metal ion to the carboxyl group which polysaccharide has with the ion bridge formation film of this invention is a minute amount. the equivalent ratio of said polyvalent metal ion to said carboxyl group -- 0.005 / 1 - 0.5/1 -- it is about 0.01 / one to 0.15/1 preferably.

[0024] GERANGAMU usually contains metal ions, such as calcium ion, with the minute amount. the equivalent ratio to the carboxyl group of the total amount of this metal ion contained beforehand and said added metal ion -- 0.061 / 1 - 0.11/1 -- it is about 0.062 / one to 0.1/1 preferably. Furthermore, even if said equivalent ratio is about 0.063 / one to 0.09/1, the tensile strength of a film can be improved greatly. In addition, if the rate of a metal ion increases, it will become easy for film reinforcement to fall. In addition, what is necessary is just to add polyvalent metal ion so that it may become said equivalent ratio when polysaccharide contains the metal component beforehand.

[0025] 1-1000 micrometers of thickness of said ion bridge formation film are about 10-500 micrometers preferably, for example. Since it softens with heating while being able to give reinforcement to a film, since the bridge is constructed over the carboxyl group of polysaccharide with the metal ion, shaping and a remolding are easy and excellent in the ion bridge formation film of this invention at recycle nature.

[0026] On said ion bridge formation film, various additives (a plasticizer, lubricant, an ultraviolet ray absorbent, an antioxidant, a bulking agent, an antistatic agent, coloring agent, etc.) etc. may be added in the range which does not check biodegradability and recycle nature. In order to raise biodegradability especially, biodegradable polymers, such as aliphatic series polyester, may be added and photolysis catalysts, such as anatase mold titanium oxide, etc. may be added. Moreover, said ion bridge formation film may be used as a laminated film with other films etc.

[0027] As long as it constructs a bridge with said metal ion and the carboxyl group of polysaccharide can be fabricated in the shape of a film, the manufacture approach of this invention is not restricted, but may cast the approach of common use, for example, the polysaccharide which has said carboxyl group, said water dissociative metallic compounds, and mixture with water, and may perform them by the approach of drying etc. Moreover, you may obtain by applying or casting, making the base material which has detachability dry the aquosity mixed liquor containing said carboxyl group content polysaccharide and metal ion by the approach of common use, for example, a roll coater, an air knife coating machine, a blade coating machine, the rod coating machine, the bar coating machine, the comma coating machine, a gravure coating machine, etc., and, for example, making it exfoliate from a base material. It is desirable to carry out film shaping especially among these film fabricating methods by the casting method [the solution casting methods (drum type, band type, etc.)].

[0028] As a solvent of a dope used for casting, you may use by the water independent, and it is the range which does not check bridge formation of the carboxyl group by polyvalent metal ion, and the organic solvent of a water miscibility may be added and used for water. As such a water miscibility organic solvent, ketones, such as alcohols, such as a methanol, ethanol, propanol, and a butanol, and an acetone, and cellosolves are mentioned, for example.
[0029] Especially the concentration of a dope is not restricted, for example, polysaccharide concentration can choose it from the range of extent preferably 0.05 to 20% of the weight 0.1 to 10% of the weight (for example, 0.5 - 5 % of the weight).
[0030]
[Effect of the Invention] In this invention, since the bridge is constructed with the metal ion in the carboxyl group of polysaccharide, high biodegradability and recycle nature can be given to an ion bridge formation film. Moreover, film reinforcement (tension breaking strength) can be greatly improved as the rate (equivalent ratio) of a metal ion to a carboxyl group is small.
[0031]
[Example] Although this invention is explained more at a detail based on an example below, this invention is not limited to these examples.
[0032] In addition, the appraisal method of the various properties of the film obtained in the example and the example of a comparison is as follows.
The piece of a film blank test (60 micrometers in 20mm[80mm by] x thickness) obtained in the [tension breaking strength] example and the example of a comparison was started, the Instron material testing machine (product made from Instron) performed the tensile test on condition that the following, and tension breaking strength was measured.
[0033]
Distance between chucks: 35mm tension rate : It is temperature by 1mm/. : 23 **1-degree-C humidity : As example polysaccharide, GERANGAMU (the Dainippon Pharmaceutical Co., Ltd. make, KERUKOGERU (trademark) (gellant gum), calcium content:5800microg/g, Mg content:1000microg/g) was used 50**5%. The calcium and magnesium which are contained in said GERANGAMU were 0.0937/1 (mole ratio) [0.0469/1 (equivalent ratio)] and 0.0266/1 (mole ratio) [0.0133/1 (equivalent ratio)] to GERAN gum unit 1mol which converts from said calcium content and Mg content, and has one carboxyl group, respectively.
[0034] In the 1-% of the weight water-solution 100 weight section of said GERANGAMU, the 0.1-% of the weight water-solution 5 weight section of calcium acetate was added, and the dope was prepared. Supply a dope to a casting machine, cast so that the thickness after drying on a base material may be set to 60 micrometers, it was made to dry for two days at 25 degrees C, and it exfoliated from the base material, and dried further (50 degrees C, 2 hours), and the ion bridge formation film was obtained. About the obtained film, tension breaking strength was measured according to said evaluation approach.
[0035] The equivalent ratio of calcium ion to the carboxyl group in a film was changed, and it evaluated like the above. The relation between the equivalent ratio of divalent metal ion (calcium ion and magnesium ion) to the carboxyl group in a film and tension breaking strength is shown in drawing 1 .
[0036] Tension breaking strength showed [the equivalent ratio / as opposed to the

carboxyl group in a film in the film of an example / of divalent metal ion] maximum in the 0.064 neighborhoods so that clearly from drawing 1 . Moreover, compared with the time of the equivalent ratio of divalent metal ion being [the equivalent ratio of said divalent metal ion] the 0.060 and 0.12 neighborhoods in the 0.064 neighborhoods, tension breaking strength is improving sharply.

CLAIMS

[Claim(s)]

[Claim 1] The ion bridge formation film whose equivalent ratio [as opposed to / the bridge is constructed over said carboxyl group with polyvalent metal ion, and / said carboxyl group] of said polyvalent metal ion it is the film which consisted of polysaccharide which has a carboxyl group, and is 0.061 / 1 - 0.11/1.

[Claim 2] The ion bridge formation film according to claim 1 whose ion bridge formation film is biodegradability.

[Claim 3] The ion bridge formation film according to claim 1 whose polysaccharide is water-soluble polysaccharide.

[Claim 4] The ion bridge formation film according to claim 1 with which polysaccharide was chosen from GERANGAMU, a carboxyl group content cellulose, carboxyl group content starch, a pectic acid, alginic acids, and these derivatives and which is a kind at least.

[Claim 5] The ion bridge formation film according to claim 1 whose polyvalent metal ion is a divalent metal ion.

[Claim 6] The manufacture approach of the ion bridge formation film which casts the polysaccharide which has a carboxyl group, a water dissociative polyvalent metal compound, and mixture with water, and is dried.

[Translation done.]

[Translation done.]